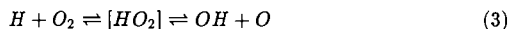*AB INITIO* POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS

Stephen P. Walch [†] and Ronald J.Duchovic [†]
Eloret Institute, Sunnyvale, CA 94087
and
Celeste McMichael Rohlfing
Sandia National Laboratories, Livermore, CA 94551-0969

NASA is currently pursuing programs of interplanetary exploration and manned flight which require a detailed understanding of the physics and chemistry occurring in hypersonic flow fields. Specifically, research efforts have focused on the bow shock layers which form in front of hypersonic vehicles and on the combustion processes of the supersonic combustion ramjet (SCRAMjet) which will power a future generation hypersonic aircraft. The chemistry of the hypersonic flow problem is particularly complex because the reactant species are expected to have non-equilibrium rovibrational distributions [1] under conditions of temperature, pressure, and flow rates which make the experimental measurement of reaction rates extremely difficult. In the case of the SCRAMjet, the short residence times make finite rate chemistry critical to the design of the engine. Consequently, the calculation of reaction rates from first principles has become an important component of the NASA research program.

Ab initio calculations designed to investigate the potential energy surfaces (PESs) of a number of reactions involving hydrogen, oxygen, and nitrogen have now been completed. In particular, the following reactions will be discussed:

$$N + O_2 \rightarrow NO + O \tag{1}$$

$$H_2 + O_2 \rightarrow H + HO_2 \tag{2}$$

$$H + O_2 \rightleftharpoons [HO_2] \rightleftharpoons OH + O \tag{3}$$

$$H + N_2 \rightleftharpoons HN_2 \tag{4a}$$

$$H + HN_2 \rightarrow H_2 + N_2 \tag{4b}$$

Reaction (1) is an important process in the high temperature chemistry of the bow shock layer created by the passage of hypersonic vehicles through atmospheres whose components include nitrogen and oxygen. Reaction (2) is an initiation step while

[†] Mailing address: NASA Ames Research Center, Moffett Field, CA, 94035

reaction (3) represents a critical chain-branching step in the H_2/O_2 combustion process. Reaction (4) is a possible two-step mechanism (chaperon mechanism) for the termolecular recombination of H atoms in the presence of N_2 ($H + H + N_2 \rightarrow H_2 + N_2$).

The calculation of reaction rates from first principles relies on both *ab initio* electronic structure theory and an appropriate dynamical theory. The first step requires the calculation of accurate approximations to the potential energy for a limited number of selected geometrical arrangements of the atoms involved in the reaction. One of several available dynamical techniques is then chosen to calculate the rate of reaction. The choice of technique is dictated both by the nature of the reaction under investigation and by the completeness of the calculated *ab initio* PES. If the calculated data is limited to the stationary points of the PES, a local representation of the PES in the neighborhood of these stationary points is determined, allowing the use of only the most elementary statistical theories to calculate the rate of reaction. If there is sufficient information to characterize accurately the minimum energy path (MEP) of the reaction, then either reaction path Hamiltonian methods or more sophisticated statistical methods can be employed in the rate calculation. Finally, if the *ab initio* data is sufficiently complete to permit the development of a global representation of the PES, then either classical trajectory or quantum scattering methods can be utilized to calculate the rate of reaction. Jaffe *et al.* will discuss the second stage of this computational procedure in a separate paper to be presented in these proceedings.

While the details of the *ab initio* computations are reported in Ref. 2-5, a brief summary of the methodology is given here. The zero-order wave function is a complete active space self-consistent field (CASSCF) wave function. For a given choice of active orbitals, every possible configuration which can be constructed by distributing the active electrons among these active orbitals is included in the wave function. The orbitals and mixing coefficients of the configuration interaction (CI) expansion are then optimized. The orbitals themselves are expanded in a finite set of atom-centered basis functions. While a basis set constructed from a segmented contraction of primitive functions was used in the study of reaction (1), the remaining calculations discussed here utilized basis functions derived from the natural orbitals of CI calculations performed on the atoms (for H atom, these calculations were performed on the H_2 molecule). The CASSCF calculation is then followed by a multireference contracted CI calculation (CCI) which allows single and double excitations from the set of reference configurations (the set of configurations which are most important in the CASSCF wave function).

Walch and Jaffe [2] have completed *ab initio* calculations for the $^2A'$ and $^4A'$ PESs of reaction (1). These calculations indicated that the $^2A'$ surface has an early barrier of 10.2 kcal/mol, while the $^4A'$ surface exhibits a barrier of 18.0 kcal/mol

(Note that none of the energies discussed in this paper include corrections for zero-point energy.). Initial global representations of these two surfaces (modified LEPS potential functions) have been constructed and used in a preliminary examination [6] of the kinetics of this reaction. Further, a more accurate functional representation of the $^2A'$ surface has been completed recently [7] and will be used in future studies supporting the development of aeroassisted orbital transfer vehicles (AOTVs).

An earlier *ab initio* study [8] of reaction (2) identified a saddle point geometry which resembles the H + HO_2 reactant configuration and a barrier of 6.3 kcal/mol. A conventional transition state theory calculation (including a Wigner tunneling correction) which treated the barrier height as an adjustable parameter required a barrier of $\approx$ 2.7 kcal/mol in order to reproduce the reaction rate measured experimentally at room temperature. The present *ab initio* calculations, using a larger basis set, estimate the barrier height to be 3.7 kcal/mol.

The MEP for H atom addition to O_2 is very similar to that found in an earlier study [9] of the same reaction. At large H–O_2 separations, the H atom initially approaches the O_2 molecule at an HOO angle of $\approx$ 119 °. This angle gradually decreases to $\approx$ 104 °, while r_{oo} gradually increases as the HO bond forms. These calculations (at the CCI level of theory) exhibit a barrier to H atom addition of $\approx$ 0.4 kcal/mol.

Two additional regions of the PES for reaction (3) which have not been studied previously were investigated in the current work. The first is the region which governs the exchange of the H atom between the two oxygen atoms. The saddle point for this process is found to be $\approx$ 13 kcal/mol below the H + O_2 asymptote, making this region of the PES accessible during the formation of $[HO_2]$ from both H + O_2 and OH + O. The second region is the OH + O channel which is complicated by the competition between a long-range classical electrostatic force (a dipole-quadrupole interaction) which favors a linear OH–O geometry, and the short-range chemical bonding interaction which favors a bent $[HO_2]$ species.

The HN_2 species (reaction (4a)) is found to lie $\approx$ 3.0 kcal/mol above the H + N_2 asymptote with a barrier of $\approx$ 12 kcal/mol between HN_2 and H + N_2. This calculated potential well contains six quasibound (harmonic) vibrational energy levels. A conventional transition state theory calculation which approximated tunneling with a one-dimensional Eckart model estimates the lifetime of HN_2 in the lowest vibrational level to be less than 6 $\times$ 10^{-9} s. This result is consistent with a recent experimental [10] estimate of less than 5 $\times$ 10^{-7} s for this lifetime.

A plot of the potential energy for reaction (4b) is shown in the figure. There are four pathways, three of which lead to stable N_2H_2 species, and a fourth which leads to H_2 + N_2. It is expected that reaction (4b) will lead to stabilized H_2 since the excess energy of the reactants can be dissipated either as relative translational
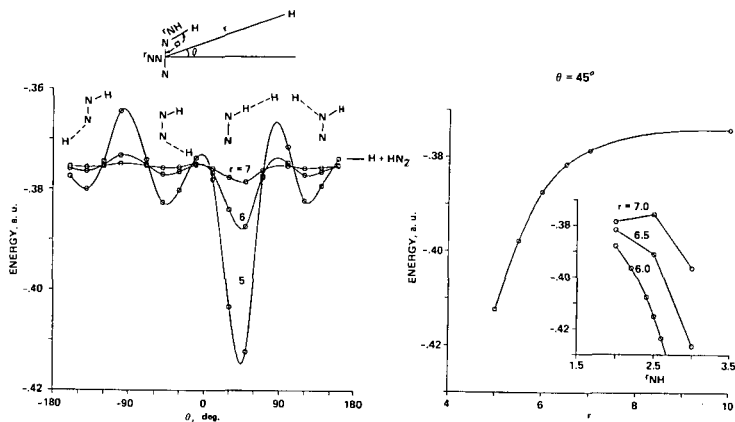
Figure 1. Plot of the potential energy for reaction (4b). In the left half of the figure the HN_2 geometry is held fixed near its optimal geometry and the H to N_2 center of mass distance, r, as well as the angle, θ, are varied. In the right half of the figure, θ is held fixed at $45°$ while r and r_{NH} are varied.

energy or rovibrational energy in the products. Because there is no potential energy barrier to the formation of $H_2 + N_2$, it might be expected that the production of H_2 will occur at or near the gas kinetic collision frequency. Estimates of the formation and dissociation rates of HN_2 combined with an estimate of the rate for reaction (4b) would yield an overall termolecular rate (chaperon mechanism) for the recombination of H atoms in the presence of N_2.

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